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14. ABSTRACT

Studies were conducted in several relevant areas, including (1) validation of the chemistry and transport models against the extinction of ultra-lean premixed hydrogen-air mixtures, (2) a comprehensive theoretical analysis of the reaction kinetics of carbon monoxide and the hydroxyl radical, (3) a theoretical kinetic study of the decomposition of ethylene oxide; (4) a gas-kinetic analysis for the transport properties of long chain molecules in dilute gases, (5) quantum-chemistry, master equation modeling of the unimolecular decomposition of ortho-benzyne, (6) extension of the previously developed hydrogen/carbon model to combustion pressures as high as 600 atm, (7) an updated kinetic mechanism of small-hydrocarbon fuel combustion for use as a kinetic foundation of higher hydrocarbon combustion, and (8) a methodology for kinetic uncertainty propagation. These projects represent the two key ingredients for meeting the overall project objectives: (a) an accurate physico-chemical property database for combustion kinetics, and (b) a unified and optimized kinetic model for liquid aliphatic and aromatic fuel combustion with quantifiable uncertainties.

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DEVELOPMENT OF A COMPREHENSIVE AND PREDICTIVE REACTION MECHANISM OF LIQUID HYDROCARBON FUEL COMBUSTION

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SUMMARY/OVERVIEW:

Studies were conducted in several relevant areas, including (1) validation of the chemistry and transport models against the extinction of ultra-lean premixed hydrogen-air mixtures, (2) a comprehensive theoretical analysis of the reaction kinetics of carbon monoxide and the hydroxyl radical, (3) a theoretical kinetic study of the decomposition of ethylene oxide; (4) a gas-kinetic analysis for the transport properties of long chain molecules in dilute gases, (5) quantum-chemistry, master equation modeling of the unimolecular decomposition of ortho-benzyne, (6) extension of the previously developed hydrogen/carbon model to combustion pressures as high as 600 atm, (7) an updated kinetic mechanism of small-hydrocarbon fuel combustion for use as a kinetic foundation of higher hydrocarbon combustion, and (8) a methodology for kinetic uncertainty propagation. These projects represent the two key ingredients for meeting the overall project objectives: (a) an accurate physico-chemical property database for combustion kinetics, and (b) a unified and optimized kinetic model for liquid aliphatic and aromatic fuel combustion with quantifiable uncertainties.

TECHNICAL DISCUSSION:

1. Validation of Chemistry and Transport Models for H_2/CO Combustion

In this collaborative project (with Professor Fokion Egolfopoulos of USC), we validated a H_2-CO kinetic model and its associated, revised transport database [1] against the extinction of premixed ultralean H_2/air flames [2]. Theoretical attention has been placed on the relative sensitivity of predicted flame extinction with respect to reaction kinetics and species diffusion coefficients. Under the conditions considered in this study, the sensitivity of diffusion coefficients on the extinction response was found to be significant and for certain species this sensitivity is greater than the kinetics rate constants. This study demonstrates the importance of an accurate transport library in the development of predictive reaction kinetic models.

This work is reported in Ref. 2.

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2. Theoretical Analysis of the CO + OH → CO$_2$ + H Reaction

In a previous study [1], we demonstrated that the currently available combustion data of H$_2$ and CO combustion cannot be reconciled unless a bi-exponential rate expression is used for the reaction CO + OH → CO$_2$ + H. While experimental evidence supports this bi-exponential temperature dependence, only a limit number of kinetic models employ such a rate expression. Theoretically the characteristic dependence of the rate constant on temperature as well as the pressure dependence remains to be carefully examined. In the present study, the rate coefficients of CO + OH → products, including the chemically activated addition/dissociation channel to produce CO$_2$ + H and the addition/stabilization reaction, are analyzed with RRKM/master equation analyses. The master equation of collision energy transfer was solved with a newly implemented Monte Carlo code. The RRKM analyses are based on the CCSD(T)/cc-pvTZ potential energy surface of Yu et al. (Chem. Phys. Lett. 2001, 349, 547-554). It is shown that over the temperature range of 80 to 2500 K and pressures from 1 Torr to 800 Bar the experimental data can be satisfactorily reproduced by lowering the CCSD(T)/cc-pvTZ energy barrier for the CO$_2$ + H exit channel by 1 kcal/mol and more importantly, by considering an equilibrium factor in the thermal rate constant formulation. This factor accounts for the populations of rovibrationally excited *trans-* and *cis*-HOCO, which are allowed to dissociate only through specific paths that are open to them. Figure 1 shows the rate constant of CO + OH → products for selected temperatures over a wide range of temperature. It is seen that the current RRKM/master equation model predicts very well the pressure dependent rate constant over a wide range of temperatures.
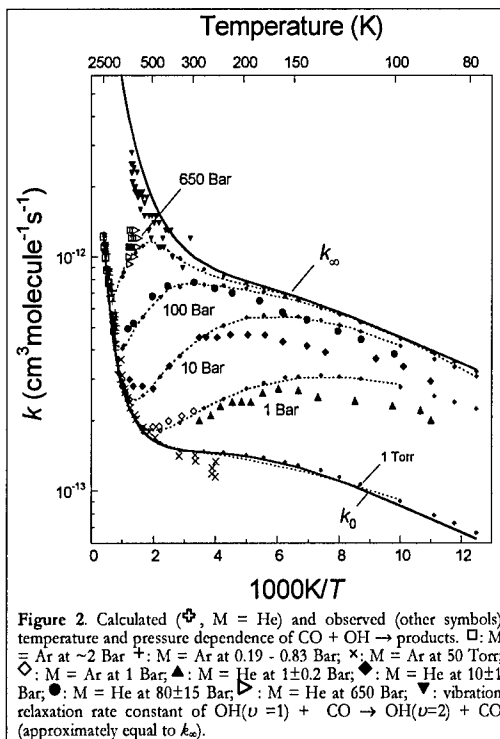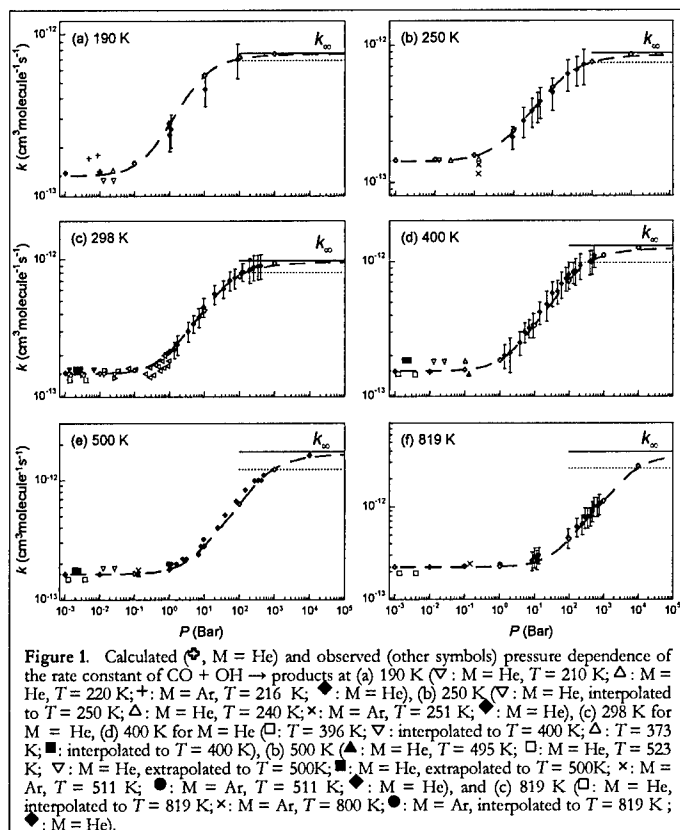
By modeling the isothermal but pressure-dependent rate data of Fulle et al. (J Chem Phys 1996, 105, 983-1000) over the temperature range from 98 to 819 K, we obtained an $\langle E_{down} \rangle$ value equal to 150 cm^{-1} for M = He. Figure 2 shows the comparison of these pressure dependent data with the predicted rate constants. The $\langle E_{down} \rangle$ values for M = N$_2$, Ar, CF$_4$ and SF$_6$ were also obtained by fitting the OH and OD data at 298 K. Based on the current theoretical analyses, we recommended that the following low-pressure limit rate expression be used for CO + OH → CO$_2$ + H,

$$k_{1b,0} \left(cm^3 molecule^{-1} s^{-1} \right) = 1.17 \times 10^{-19} T^{2.053} \exp\left(\frac{139}{T} \right) + 9.56 \times 10^{-12} T^{-0.664} \exp\left(-\frac{167}{T} \right).$$

The above expression is valid for temperature from 120-2500 K. In addition, for P (Bar) < $9 \times 10^{-17} T^{5.9} \exp(520/T)$, the rate constant is practically at the low pressure limit. Fall-off parameterization is also proposed over the entire range of pressure for the rate coefficients of CO + OH → CO$_2$ + H and CO + OH → HOCO over the temperature range from 120 to 2500 K..

For 800 K < T < 2500 K the theoretical rate expression given above agrees remarkably well with the same rate obtained by optimizing our recent H$_2$/CO model [1] against the available combustion data (<5% difference). In addition, the current theoretical analysis shows that for combustion applications the pressure dependence of the rate constant for CO + OH → CO$_2$ + H is negligible since for T > 1200 K the low-pressure expression given above is valid for pressure < 200 Bar.

This work is reported in Ref. 3.

Figure 1. Calculated ($\oplus$, M = He) and observed (other symbols) pressure dependence of the rate constant of CO + OH → products at (a) 190 K ($\triangledown$: M = He, T = 210 K; $\triangle$: M = He, T = 220 K; +: M = Ar, T = 216 K; ◆: M = He), (b) 250 K ($\triangledown$: M = He, interpolated to T = 250 K; $\triangle$: M = He, T = 240 K; ×: M = Ar, T = 251 K; ◆: M = He), (c) 298 K for M = He, (d) 400 K for M = He ($\square$: T = 396 K; $\triangledown$: interpolated to T = 400 K; $\triangle$: T = 373 K; ■: interpolated to T = 400 K), (b) 500 K (▲: M = He, T = 523 K; $\triangledown$: M = He, extrapolated to T = 500K; ■: M = He, extrapolated to T = 500K; ×: M = Ar, T = 511 K; ●: M = Ar, T = 511 K; ◆: M = He), and (c) 819 K ($\square$: M = He, interpolated to T = 819 K; ×: M = Ar, T = 800 K; ●: M = Ar, interpolated to T = 819 K; ◆: M = He).

Figure 2. Calculated ($\oplus$, M = He) and observed (other symbols) temperature and pressure dependence of CO + OH → products. $\square$: M = Ar at ~2 Bar +: M = Ar at 0.19 - 0.83 Bar; ×: M = Ar at 50 Torr; $\lozenge$: M = Ar at 1 Bar; ▲: M = He at 1±0.2 Bar; ◆: M = He at 10±1 Bar; ●: M = He at 80±15 Bar; $\triangleright$: M = He at 650 Bar; ▼: vibration relaxation rate constant of OH(v =1) + CO → OH(v=2) + CO (approximately equal to k_∞).

3. Reaction Kinetics of Ethylene Oxide Decomposition

The unimolecular decomposition of ethylene oxide and the oxiranyl radial is examined by molecular orbital calculations, Rice-Ramsperger-Kassel-Marcus (RRKM)/Master Equation analysis, and detailed kinetic modeling of ethylene oxide pyrolysis in a single-pulse shock tube. The study was motivated by the need to better understand the kinetics of reactions involving spin state crossing. The development of this model was also made in response to the need of the Wright-Patterson research lab for a reliable reaction model for ethylene oxide combustion.

It was found that the largest energy barrier to the decomposition of ethylene oxide lies in its initial isomerization to form acetaldehyde, and in agreement with previous studies, the isomerization was found to proceed through the $\cdot$CH$_2$CH$_2$O $\cdot$ biradical. Because of the biradical nature of the transition states and intermediate, the energy barriers for the initial C-O rupture in ethylene oxide and the subsequent 1,2-H shift remain highly uncertainty (see, Figure 3). On the other hand, an overall isomerization energy barrier of 59 ± 2 kcal/mol was found to satisfactorily explain the available single pulse shock tube data (Figure 4). This barrier height appears to be in line with the estimates made from an approximate spin-corrected procedure at the MP4/6-31+G(d) and QCISD(T)/6-31G(d) levels of theory.

The high pressure limit rate constant for the unimolecular decomposition of ethylene oxide was calculated as

$$k_{1,\infty}\left(1/s\right) = 3.74 \times 10^{10}\ T^{1.298} e^{-29990/T}\ \text{for } 600 < T < 2000\ \text{K}.$$

The dominant channel for the unimolecular decomposition of ethylene oxide was found to form CH_3 + HCO, and at the ambient pressure and for $T > 800$ K it accounts for >90% of the total rate constant.

The present work constitutes a step forward in our understanding of the singlet manifold of the C_2H_4O potential energy surface. A combination of this singlet PES with that of the triplet states is required to address the chemistry of the O + C_2H_4 reaction. This combination of the surfaces requires calculations of the spin-orbit coupling between the singlet and triplet ring-opened $\cdot CH_2CH_2O \cdot$ biradicals. We are hopeful that, with the singlet surface now well understood, we will

Figure 3. Potential energy barriers of the ethylene oxide system, determined at the G3 level of theory. The dashed line represents an approximation for the initial isomerization step.

Figure 4. Comparison of predicted (lines) and experimental (symbols, [8]) concentration profile of ethylene during shock tube pyrolysis of ethylene oxide (dwell time = 2 ms). Computations were carried out for Mixture A (solid lines) and Mixture C (dashed lines).

be able to accurately predict the branching rations and the respective rate constants for the reaction of O + C_2H_4.

This work is reported in Ref. 4.

4. Transport Theory of Long Chain Molecules in Dilute Gases

One of the major theoretical hurdles to obtain a quantitative understanding of the combustion chemistry of jet fuels and their surrogates is the lack of a suitable theory to describe the diffusion coefficient of long chain aliphatic molecules. Although the Chapman-Enskog theory is traditionally employed to calculate the binary diffusion coefficient, its underlying assumption of spherical potentials for the collision pair renders the applicability of the theory questionable. In this work, a rigorous, gas-kinetic theory analysis was carried out, and analytical equations are developed for the diffusion coefficient of long-chain molecules in the limits of specular and diffuse scattering.

A long-chain molecule may be approximated as a straight and rigid cylinder. Consider a cylinder with length equal to L and diameter D. Gas-kinetic theory analysis shows that the instantaneous drag force due to relative motion of a cylinder in a dilute gas may be given by

$$F_{s/d} = \frac{1}{2}\sqrt{\left(1 + 5\sin^2 \alpha / 4\right) 2\pi m_r kT} NLDV \Omega_{s/d}^{(1,1)*} \tag{1}$$

4

where the subscript "s/d" denotes specular or diffuse scattering, α is the angle of the cylinder relative to the flow, m_r is the reduced mass, k is the Boltzmann constant, T is the temperature, N is the gas number density, V is the relative velocity. In eq. (1) $\Omega_s^{(1,1)*}$ is the reduced collision integral given by

$$\Omega_{s/d}^{(1,1)*} = \frac{\int_0^\infty \gamma^5 \exp\left(-\gamma^2\right) \mathcal{Q}_{s/d}\left(g\right) d\gamma}{LD} \tag{2}$$

where $\mathcal{Q}_{s/d}(g)$ is the collision cross section, defined in the two limiting scattering scenario as

$$\mathcal{Q}_s\left(g\right) = L \int_{-\infty}^{\infty} \left(1 - \cos\chi\right) db, \tag{3a}$$

and

$$\mathcal{Q}_d\left(g\right) = L \left[\begin{array}{l} \int_{-b_0}^{b_0} \left(1 + \frac{1}{g}\sqrt{\frac{\pi kT}{2m_r}} \sin\frac{\chi}{2}\right) db \\ + \int_{b_0}^{\infty} \left(1 - \cos\chi\right) db + \int_{-\infty}^{-b_0} \left(1 - \cos\chi\right) db \end{array} \right], \tag{3b}$$

respectively. In eqs (3), the angle χ is given by

$$\chi\left(g,b\right) = \pi - 2b \int_{r_m}^{\infty} \frac{dr}{r^2 \sqrt{1 - \frac{b^2}{r^2} - \frac{\Phi\left(r,L\right)}{m_r g^2/2}}} \tag{4}$$

where r is the center-to-axial distance between the gas molecule and cylinder, r_m is the distance of the closest encounter, and $\Phi\left(r,L\right)$ is the potential function between the gas molecules and cylinder. In the limit of rigid-body collision, it may be shown that

$$\Omega_s^{(1,1)*} = 4/3 \tag{5a}$$

and

$$\Omega_d^{(1,1)*} = 1 + 3\pi^2/64. \tag{5b}$$

Realistically molecular scattering always lies between the two limiting scattering models. Similar to the treatment of nanoparticle transport, a parameter may be introduced here to give a mixed scattering model, such that an average, reduced collision integral may be defined as

$$\Omega_{avg}^{(1,1)*} = \varphi\Omega_s^{(1,1)*} + \left(1-\varphi\right)\Omega_d^{(1,1)*}, \tag{6}$$

where φ is termed as the momentum accommodation function, which ranges from 0 to 1. From the knowledge of gas-nanoparticle scattering, it may be speculated that for long-chain aliphatic molecules φ is close to unity [5].

The instantaneous binary diffusion coefficient of a cylinder in a dilute gas may be obtained from the Stokes-Einstein relation, through the drag coefficient, as

$$D_{12} = 2\sqrt{\frac{kT}{\left(1 + 5\sin^2\alpha/4\right)2\pi m_r}} \frac{1}{NLD\Omega_{avg}^{(1,1)*}} \cdot \tag{7}$$

An angle-averaged diffusion coefficient is obtained by replacing α by the mean angle $\overline{\alpha}$ of the orientation of the cylinder with respect to its diffusion direction.

The remaining work will be (a) to examine the potential function $\Phi(r,L)$ and to determine a suitable, parameterized form for this function, and (b) to carry out suitable experiments to determine the diffusion coefficients of representative, long-chain aliphatic molecules. Both components of the study are required to validate the theory developed.

5. Kinetics of unimolecular decomposition of *ortho*-benzyne

The kinetics of *ortho*-benzyne is an integral part of aromatics oxidation at high temperatures. Previously, it was concluded that the dominant channel of *ortho*-benzyne decomposition is through the concerted unimolecular dissociation leading to diacetylene and acetylene,

$$o\text{-}C_6H_4 \rightarrow C_2H_2 + C_4H_2 . \tag{8}$$

Recent shock-tube studies at DLR suggest that an additional reaction channel may become active at temperatures > 1600 K. This channel is characterized by the production of the H atom,

$$o\text{-}C_6H_4 \rightarrow C_6H_2 + 2H \tag{9}$$

The shock tube study used 1,2-diiodobenzene is the precursor for *ortho*-benzyne.

In this study, we examined the potential energy surface of *ortho*-benzyne decomposition by molecular orbital calculations. The computation was carried out at the CCSD(T)/6-31G(d)//B3LYP/6-31G(d) level of theory. The minimum energy barrier for H production was computed to be 106 kcal/mol from *ortho*-benzyne. This energy barrier renders direct H production implausible below 2000 K. Subsequently, the reaction rate coefficient was analyzed by master equation modeling. Kinetic modeling shows that below 2000 K the apparent production of the H atom is due to the decomposition of the precursor compound, rather than the decomposition of *ortho*-benzyne. The work is reported in Ref. 6.

6. H₂/CO combustion up to 600 atm

This is a collaborative research project with Professor Brezinsky at UIC. In this study, the high pressure oxidation of dilute CO mixtures doped with 150-200 ppm of H_2 has been studied behind reflected shock waves in the UIC high pressure single pulse shock tube. The experiments were performed over the temperature range from 1000-1500 K and pressures spanning 21-500 bars for stoichiometric ($\Phi=1$) and fuel lean ($\Phi=0.5$) oxidation. Stable species sampled from the shock tube were analyzed by standard GC, GC/MS techniques. The experimental data obtained were simulated using a previously published detailed model for H_2/CO combustion. Simulations showed that within experimental error the kinetic model was able to capture the experimental trends for the lower pressure data sets (average nominal pressures of 24 and 43 bars). However the model under predicts the CO and O_2 decay and subsequent CO_2 formation for the higher pressure data sets (average nominal pressures of 256 and 450 bars). The current elevated pressure data sets span a previously

unmapped regime and have served to probe HO_2 radical reactions which appear to be among the most sensitive reactions in the model under these conditions. With updated rate parameters for $HO_2 + OH = O_2 + H_2O$ the model is able to reconcile the elevated pressure data sets thereby extending the capability of the reaction model to an extreme range of conditions.

This work is reported in Ref. [7].

7. Updated C_1-C_4 Reaction Model

The need to re-evaluate our previous C_1-C_4 kinetic model stems from the fact that its H_2/CO submodel had to be revised because of the recent downward revision of the heat of formation of the OH radical and new kinetic data of $H + O_2$ (+M) $\rightarrow$ HO_2 (+M) made available only recently [1]. Currently we have completed a re-evaluation of relevant kinetic rate constants and thermochemical data. Emphasis is placed on quantify the uncertainty factors for all rate coefficients. Concurrently, we are exploring new, modularized optimization methods, which will allow future revision of the kinetic submodels be made and its optimization done in an isolated fashion. The resulting model will have the capability to examine uncertainty propagation, a component critically needed to extend the kinetic foundation model to large hydrocarbons.

8. Methodology of kinetic uncertainty propagation

We begin to develop a mathematical procedure to propagate kinetic uncertainty into combusting flow simulations. Figure 1 shows the statistical distributions of CO_2 mass fraction of ethylene oxidation in air in a perfectly stirred reactor ($\phi = 1.0$, $T = 1400$ K and $p = 1$ atm) as a function of the residence time τ. These distributions were obtained by Monte Carlo simulations. Although they nicely predict the wide distributions under the conditions where the residence time is limited, and the bifurcation of the distribution near the turning points, Monte Carlo simulations are inherently expansive. Currently, we are looking at a suitable mathematical procedure by which these distribution functions can be computed directly. A part of this work is to be reported in Ref [8].

Figure 5. Statistical distributions of PSR solutions for the CO_2 mass fraction (C_2H_4-air mixture, $\phi = 1.0$, $T = 1400$ K and $p = 1$ atm).
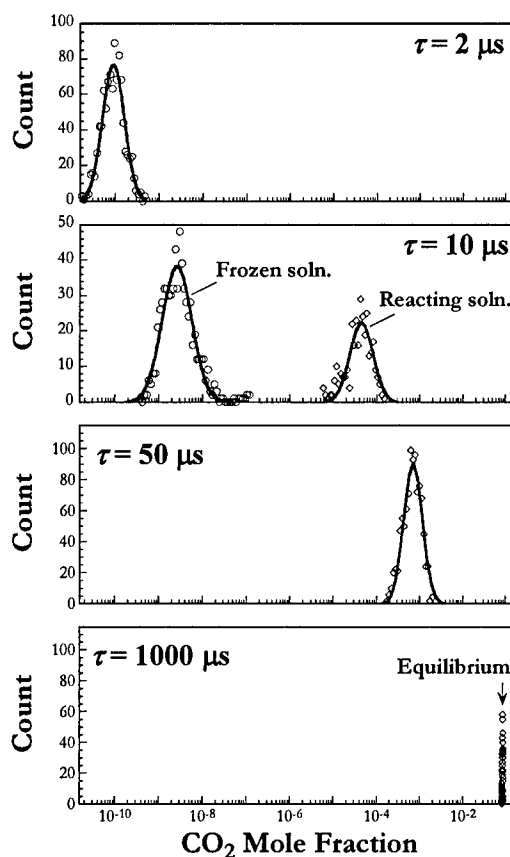
EXTRAMURAL-INTRAMURAL INTERACTIONS

Our AFRL contact person is Dr. J. T Edwards. Several visits to the Wright-Patterson AFRL were made during the project period. During the visit, the PI discussed potential research collaborations with various lab research personnel, and gave a seminar entitled "Incipient Soot Formation and Growth." We also worked closely with Drs. Dean Eklund and Skip Williams and delivered a pseudo-detailed ethylene oxidation mechanism for Scamjet simulations.

PERSONNELL SUPPORTED

Hai Wang, PI (one-summer month salary)
Xiaoqing You (graduate student)

TECHNOLOGY ASSISTS, TRANSITIONS AND TRANSFERS

Performer: Dr. Hai Wang, University of Southern California
Customer: Dr. Chris Montgomery, Reaction Engineering International, 77 West 200 South Suite 210, Salt Lake City, Utah 84101.
Result: Improved reaction model of small hydrocarbon combustion
Application: CFD simulation of combustion in gas turbines.

AFOSR SPONSORED PUBLICATIONS AND PRESENTATIONS:

1. Davis, S. G., Joshi, A. V., Wang, H., and Egolfopoulos, F., "An optimized kinetic model of H_2/CO combustion," *Proceedings of the Combustion Institute*, **30**, pp. 1283-1292 (2005).

2. Dong, Y., Holley, A. T., Andac, M. G., Egolfopoulos, F. N., Davis, S. G., Middha, P., and Wang, H. "Premixed extinction of H_2/air flames: chemical kinetics and molecular diffusion effects." *Combustion and Flame*, **142**, pp.374-387 (2005).

3. Joshi, A. V. and Wang, H. "Master equation modeling of wide temperature and pressure dependence of CO + OH → products." *International Journal of Chemical Kinetics*, **38**, pp. 57-73 (2006).

4. Joshi, A. V., You, X., Barckholtz, T., and Wang, H., "Thermal decomposition of ethylene oxide: potential energy surface, master equation analysis and detailed kinetic modeling." *Journal of Physical Chemistry A* **109**, pp. 8016-8027 (2005).

5. Li Z. and Wang, H. "Gas-nanoparticle scattering: A molecular view of momentum accommodation function." *Physical Review Letters*, **95**, paper 014502 (2005).

6. Chen, X., You, X., Braun-Unkhoff, B., Naumann, C., Frank, P., Just, T., and Wang, H. "Shock tube pyrolysis of 1,2-diiodobenzene–kinetics of H atom production in high-temperature thermal decomposition of *ortho*-benzyne." poster paper presented at *the 6th International Conference of Chemical Kinetics*, National Institute of Standards and Technology, Gaithersburg, Maryland, July 25-29, 2005.

7. Sivaramakrishnan, R., Comandini, A., Tranter, R. S., Brezinsky, K., Davis, S. G. and Wang, H. "Combustion of CO/H_2 mixture at elevated pressures," *Proceedings of the Combustion Institute*, **31**, pp. 429-437 (2007).

8. Sheen, D., Wang, H. "Expansion analysis of kinetic model uncertainty beyond parameter optimization," the Fifth Joint States Section of the Combustion Institute Meeting, San Diego, CA, March 25-28, 2007, paper 07-P24.

9. Middha, P. and Wang, H. "First-principle calculation for the high-temperature diffusion coefficients of small pairs: the H-Ar case." *Combustion Theory and Modeling* **9**, pp. 353-363 (2005).